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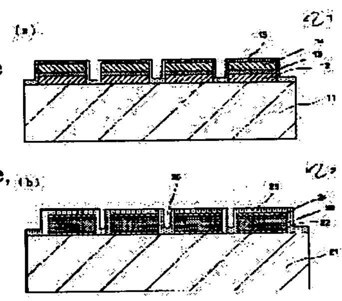
(54) ELECTRODE SUBSTRATE

(57)Abstract:

PROBLEM TO BE SOLVED: To improve moisture resistance while keeping high transmissivity and improve moisture resistance while keeping high reflectance index by arranging an insulating film of which the refractive index is larger than a specified value on a three-layer electrode.

SOLUTION: For an electrode base board 1, a three-layer electrode is made of glass board 11, a transparent oxide film 12 as a stripe-pattern-shaped transparent electrode, a silver film 13, and a transparent oxide film 14. An insulating film 15 being cerium oxides is made to cover the pattern of this three-layer electrode, and this is made an electrode based board 1. Moisture resistance can be improved while keeping high transmissivity and moisture resistance can be improved while keeping high reflectance, by arranging it on the three- layer electrode, enlarging the refractive index of the insulating film 15 more than 2.1.



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CLAIMS

[Claim(s)]
[Claim 1] The electrode substrate characterized by coming to arrange an insulator layer with a larger refractive index than 2.1 on the above-mentioned electric conduction film in the electrode substrate equipped with the electric conduction film of a configuration of pinching a silver system thin film with a transparence oxide thin film on a substrate.
[Claim 2] The electrode substrate according to claim 1 characterized by the base material of the above-mentioned insulator layer being cerium oxide.
[Claim 3] The electrode substrate according to claim 1 or 2 characterized by being in the range whose thickness of the above-mentioned insulator layer is 1nm - 70nm.
[Claim 4] The electrode substrate according to claim 1, 2, or 3 characterized by being in the range whose thickness of the above-mentioned silver system thin film is 4nm - 17nm.
[Claim 5] The electrode substrate according to claim 1, 2, or 3 characterized by being in the range whose thickness of the above-mentioned silver system thin film is 50nm - 200nm.
[Claim 6] The electrode substrate according to claim 1, 2, 3, 4, or 5 with which the base material of the above-mentioned transparence oxide thin film is characterized by being the mixed oxide of cerium oxide and indium oxide.
[Claim 7] The electrode substrate according to claim 1, 2, 3, 4, or 6 characterized by arranging the color filter between the above-mentioned substrate and the electric conduction film.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] With respect to the transparent electrode or reflector the electrode substrate of transparent electrodes for displays, such as a liquid crystal display, an I/O device, or a plasma display, or a reflector, or for solar batteries, especially this invention has conductivity and high visible-ray permeability at a thin film, and relates to the electrode substrate which was moreover excellent in preservation stability.
[0002]
[Description of the Prior Art] The electrode plate with which the transparence electric conduction film of the electrode configuration which penetrates a visible ray was prepared on substrates, such as glass and plastic film, is widely used for the I/O electrode which carries out a direct input from the display screen of the electrode for a display of various displays, such as a liquid crystal display, or this display. For example, the transparent electrode plate of the display unit with which liquid crystal was used The color filter layer 37 which is prepared in the pixel part on a glass substrate 31 and this glass substrate 31, and colors that transmitted light red, green, and blue for

every pixel, respectively as shown in drawing 2 , The light-shielding film 38 which is prepared in the part between the pixels on the above-mentioned glass substrate 31 (about pixel Mabe), and prevents the light transmission from this part, That principal part consists of a protective layer 39 prepared all over the above-mentioned color filter layer 37, a transparent electrode 40 formed on this protective layer 39, and orientation film 41 formed on this transparent electrode 40. And membranes are formed by sputtering and the above-mentioned transparent electrode 40 is constituted by the transparence electric conduction coat etched into the predetermined pattern.
[0003] The ITO thin film which added tin oxide in indium oxide as this transparence electric conduction coat paying attention to that high conductivity is used widely, that specific resistance is 2.4x10-4 ohm-cm about, and, in the case of the 240nm thickness usually applied as a transparent electrode, that sheet resistivity is about 10ohm/**. Moreover, although the tin oxide thin film, the thin film (Nesa membrane) constituted by this tin oxide by adding antimony oxide, the thin film constituted by the zinc oxide by adding an aluminum oxide are known in addition to this, each of these is inferior to the above-mentioned ITO thin film in that conductivity, and since chemical resistance or a water resisting property to an acid or alkali etc. is inadequate, generally they has not spread.
[0004] The transparence electric conduction film of the three-tiered structure which the front rear face of a silver thin film is made to carry out the laminating of an ITO thin film or the indium oxide thin film (IO thin film) as heat ray reflective film, and is constituted in the 7thICVM held in Japan in 1982 on the other hand is proposed. The transparence electric conduction film of this three-tiered structure has sheet resistivity with low about 5ohms / ** extent, and the application to the above-mentioned transparent electrode was expected taking advantage of that high conductivity.
[0005]
[Problem(s) to be Solved by the Invention] By the way, in the above-mentioned display unit or the I/O device, it is required that increasing a pixel consistency and displaying a precise screen in recent years should be called for, and the eburnation of the above-mentioned transparent electrode pattern should be demanded in connection with this, for example, the terminal area of the above-mentioned transparent electrode should be constituted from a pitch which is about 100 micrometers. Moreover, in the method (COG) with which direct continuation of the IC for a liquid crystal drive is carried out to a substrate in liquid crystal display equipment, there is a part from which leading about of wiring serves as a thin line called width of face of 20-50 micrometers, and the advanced etching processing suitability which is not in the former, and high conductivity (low resistivity) are demanded.
[0006] Moreover, in order to also call for enlargement of the display screen on the other hand, to form the transparent electrode of a precise pattern which was mentioned above about such big screen-ization and to enable it to impress sufficient driver voltage for liquid crystal moreover, the transparence electric conduction film equipped with the high conductivity below 5ohms / **, as the above-mentioned transparent electrode needed to be applied. moreover -- in addition, when performing the multi-gradation display of 16 or more gradation in the liquid crystal display of the passive-matrix drive method using STN LCD etc., low sheet resistivity is demanded of the pan below 3ohms / **.
[0007] However, also in the transparence electric conduction film of the above-mentioned three-tiered structure proposed in the 7thICVM, the sheet resistivity of at most 5ohms / ** extent did not pass to be obtained, but there was a trouble that sufficient conductivity was not securable. In addition, although it is possible to reduce the sheet resistivity to about 3ohms / ** by making thickness of a silver thin film thick to about 16-18nm, visible-ray permeability (especially a long wave with a wavelength of about 610nm visible-ray permeability by the side of merit) will fall to about 75%, and the function as transparence electric conduction film will be spoiled.
[0008] furthermore, the moisture in the air into which the silver thin film advanced from the laminating interface etc. in the transparence electric conduction film of the above-mentioned three-tiered structure -- combining -- easy -- the front face -- a reactant -- generating -- silverfish -- when the defect of a ** was produced, for example, it applied to the transparent electrode of a liquid crystal display, the trouble of being easy to produce a display defect etc. was shown in the front face. It is in offering the transparence electric conduction film which this invention is made paying attention to such a trouble, and conductivity and whose visible-ray permeability are [the place made into the technical problem] high at a thin film, moreover does not have degradation with the passage of time, and was excellent in preservation stability.
[0009] On the other hand, in the transparent electrode for solar batteries, hydrogen plasma resistance is needed due to the manufacture process. For this reason, it is common to use the transparent electrode which uses a zinc oxide with high hydrogen plasma resistance as a base material. However, what carried out the fluorine dope, and the thing which carried out alumina addition also had high resistance, and the transparent electrode of a zinc-

oxide system needed to form it in 400nm - 800nm and quite thick thickness as a transparent electrode for solar batteries.

[0010] this invention persons have proposed the electrode substrate in which the electric conduction film of a configuration of pinching the silver system thin film which considers as the electrode substrate which can solve these problems mostly, for example, contains 0.1-3at% copper with a transparence oxide thin film was formed. However, although practical use level had this configuration mostly, its moisture resistance was a little inadequate. copper -- 1at% -- when the electrode substrate with the electric conduction film (it abbreviates to a three-layer electrode hereafter) of a configuration of pinching the silver system thin film to contain with a transparence oxide thin film was kept under the high-humidity/temperature environment of 60 degrees C and 95% humidity, the problem which minute silverfish generates was in the pattern before or after about 200 hours.

[0011]

[Means for Solving the Problem] When this invention persons repeated examination wholeheartedly in view of the above technical technical problems, it discovered obtaining a result with the sufficient configuration which formed the insulator layer which is excellent in a high refractive index and chemical resistance on the three-layer electrode as a protective coat. About a refractive index, a similarly high thing is desirable also in the transparence oxide thin film which pinches not only a protective coat but a silver system thin film. In the case of the three-layer electrode of the gestalt which touches a liquid crystal ingredient (the refractive index of the usual liquid crystal is 1.5 to about 1.6) and a color filter (extent to which the refractive index of the ingredient of a color filter exceeds 1.5 a little) with a refractive index higher than air, this inclination is remarkable.

[0012] For example, although B line of drawing 4 shows a simulation result in case one side of the three-layer electrode formed on substrates, such as glass, is air, in permeability T, a reflection factor R falls 96% or more at a peak till the place near 1%. Here, thickness of the transparence oxide thin film of the side which touches 40nm in the thickness of the transparence oxide thin film by the side of a substrate, and touches 14nm and air in Ag thickness was set to 44nm. The refractive index of a transparence oxide thin film was calculated as the 2.0 [almost same] as ITO. However, 40nm laminating of the orientation film of polyimide is carried out on a three-layer electrode, and if the refractive index of the liquid crystal which touches this is recalculated as 1.5, as shown in A of drawing 4 , permeability T and a reflection factor R will get quite bad. The peak of permeability will be less than 90%, and a reflection factor R will rise to about 10% near the wavelength of 550nm of light.

[0013] From this, this invention persons changed the refractive index of a transparence oxide thin film, and performed count in the form where the polyimide film and liquid crystal as orientation film of liquid crystal touch a three-layer electrode (while changing the refractive index, the thickness of the transparence oxide thin film which pinches a silver system thin film was also adjusted, and it optimized mostly). A result is shown in drawing 3 . It turns out that permeability will improve if the one where the refractive index of a transparence oxide thin film is higher exceeds especially 2.1, and a reflection factor also falls.

[0014] Thus, this invention persons have found out that optimization of the permeability is possible in the three-layer electrode by adjusting the thickness of a transparence oxide thin film corresponding to the thickness of a silver system thin film. this invention persons discovered further that this transparence oxide thin film could replace a part by the insulator layer of a high refractive index. It discovered collectively that the dependability of a three-layer electrode improved greatly by the replacement by the insulator layer. That is, invention concerning claim 1 is an electrode substrate characterized by coming to arrange an insulator layer with a larger refractive index than 2.1 on the above-mentioned electric conduction film in the electrode substrate equipped with the electric conduction film of a configuration of pinching a silver system thin film with a transparence oxide thin film on a substrate.

[0015] Cerium oxide has the very high refractive index of about 2.5 also for strong alkali resistance in coincidence suddenly. In the form where it substitutes for a part of thickness of a transparence oxide thin film, the insulator layer which uses cerium oxide as a base material can be used. That is, invention concerning claim 2 is an electrode substrate according to claim 1 characterized by the base material of an insulator layer being cerium oxide. In cerium oxide, the oxide of other metals (or semimetal), such as tantalum oxide which is rich in acid-proof and alkali resistance, and an oxidation gallium, tin oxide, may be added.

[0016] It is appropriate for formation of an insulator layer to set the thickness as the range of 1nm - 70nm. Although it may be thinner than 1nm, if it takes into consideration in accordance with the effectiveness (the configuration will tend to be destroyed by moisture etc. with this as the starting point if a three-layer electrode has a minute defect) of burying the thickness control at the time of membrane formation, and the defective part of a three-layer electrode, 1nm is required at least. Consideration of permeability and a reflection factor of the

thickness of one side of the transparence oxide thin film of a three-layer electrode chooses it from the range of 20nm - 70nm in general. The maximum thickness of an insulator layer is good at 70nm noting that it substitutes for the transparence oxide thin film in an insulator layer. That is, it is the electrode substrate according to claim 1 or 2 characterized by the range whose thickness of an insulator layer is 1nm - 70nm having invention concerning claim 3.

[0017] As a result of repeating research still more deeply, this invention persons found out that there was suitable range for the thickness of a silver system thin film, when the refractive index of a transparence oxide thin film was made high. The simulation result at the time of setting the refractive index of a transparence oxide thin film to 2.3, and setting [the thickness of the transparence oxide thin film by the side of a glass substrate (n= 1.5) / the thickness of 35nm and a silver system thin film / the thickness of 12nm and the upper transparence oxide thin film] the refractive index of 40nm and a medium (liquid crystal is assumed) to 1.5 for the thickness of 37nm and the polyimide film was shown in drawing 5 . The thinner one of the thickness of a silver system thin film has high permeability, and a reflection factor becomes low and shows the good inclination. When the thickness of a silver system thin film becomes thicker than 17nm, it turns out that it becomes difficult, as for permeability with a wavelength [of light] of 550nm, to maintain 90% or more, and there is the need of forming more thinly than 17nm. Moreover, if a silver system thin film is made thinner than 4nm, the homogeneous film will be hard to be formed in practice, and it will turn into island-like film deposition. When thinner than 4nm, since a reflection factor increases by such reason, as for the thickness of a silver system thin film, it is desirable to make it thicker than 4nm. In addition, of course with the configuration which uses the light source of high brightness as a back light a premise [the transparency mold LCD], a silver system thin film may be thickly formed from 17nm. That is, it is the electrode substrate according to claim 1, 2, or 3 characterized by the range whose thickness of a silver system thin film is 4nm - 17nm having invention concerning claim 4.

[0018] Moreover, in a three-layer electrode, if the thickness of a silver system thin film is formed more thickly than 50nm, it will become a reflector with the high reflection factor of light. A reflector can be used as the reflector which served both as the reflecting plate and the drive electrode with the reflective mold liquid crystal display, or reflective film of the light which is a solar battery, and is formed in a semiconductor device rear face in order to raise photoelectric conversion efficiency. 2.3 is carried out for the refractive index of 1.5 and a transparence oxide thin film, and drawing 6 carries out [the refractive index which is a medium] simulation of the thickness of a silver system thin film for thickness as 50nm, 75nm, 100nm, and 200nm in 40nm. If the thickness of a silver system thin film exceeds 50nm, it will become a reflexibility electrode around 80%, and a reflection factor is saturated with 200nm, and it is shown that permeability also becomes about 0%. That is, it is the electrode substrate according to claim 1, 2, or 3 characterized by the range whose thickness of a silver system thin film is 50nm - 200nm having invention concerning claim 5.

[0019] In addition, although the substrate which forms a reflector may be transparent, it may be a substrate colored the color of white, and black and others. The quality of the material can also use various things, such as a substrate with which the semiconductor device of glass, plastic film, a ceramic, a metal, or an amorphous silicon was formed.

[0020] By the way, the conventional three-layer electrode represented by the configuration of [ITO/Ag/ITO] has a big problem in moisture resistance. Moreover, since a refractive index is 1.8 to about 2.0, ITO cannot offer the three-layer electrode of high performance. this invention persons found out that the configuration using the mixed oxide of cerium oxide and indium oxide as a transparence oxide thin film of a three-layer electrode was extremely excellent in moisture resistance and an optical property, as a result of examining various oxide. That is, it is the electrode substrate according to claim 1, 2, 3, 4, or 5 with which invention concerning claim 6 is characterized by the base material of a transparence oxide thin film being the mixed oxide of cerium oxide and indium oxide.

[0021] The transparence oxide thin films by this mixed oxide are the metallic element conversion (an oxygen element is not counted) contained as an oxide, and can offer the electrode substrate mostly equipped with the electric conduction film of practical use level for a cerium element as a three-layer electrode more than 5at% and by adding to more than 20at% and indium oxide preferably. When pattern formation is required as a three-layer electrode and it is premised on wet etching, as for the addition of a cerium element, less than [40at%] is good. When it comes to more than 40at%, the pattern formation in wet etching becomes a little difficult. In the case of dry etching, this problem does not exist at the addition beyond 40at%, either. Moreover, when pattern formation is unnecessary, it is good also as a mixed oxide in the level which exceeds 40at(s)% for a cerium element. The refractive index of a transparence oxide thin film turns into a high refractive index as the rate of cerium oxide becomes high. It was [in this invention persons' data] n= 2.49 at n= 2.30 and 100at% in n= 2.24 and 40at% by n=

2.17 and 30at% at cerium 20at%. In addition, these refractive indexes are influenced according to the partial pressure of the oxygen gas at the time of membrane formation, the annealing temperature conditions after membrane formation, etc.

[0022] The electrode substrate by this invention makes color display possible by arranging the color filter colored red, green, blue, etc. between a substrate and the three-layer electrode which is a transparent electrode, when using as an electrode substrate for displays. That is, invention concerning claim 7 is an electrode substrate according to claim 1, 2, 3, 4, or 6 characterized by arranging the color filter between a substrate and the electric conduction film.

[0023]

[Embodiment of the Invention] The gestalt of operation of this invention is stated to the following examples.

[0024]

[Example] Hereafter, the example of this invention is explained to a detail with reference to a drawing.

<Example 1> the electrode substrate 1 concerning this example As shown in drawing 1 (a), as the glass substrate 11 with a thickness of 0.7mm and a stripe pattern-like transparent electrode The transparence oxide thin film 12 with a thickness of 40nm, The silver system thin film 13 with a thickness of 15nm, the transparence oxide thin film 14 with a thickness of 40nm, and the insulator layer 15 that is cerium oxide with a thickness of 2nm as the pattern of this three-layer electrode is covered were formed, and it considered as the electrode substrate for liquid crystal displays.

[0025] the transparence oxide thin films 12 and 14 -- each -- metallic element conversion (an oxygen element is not counted) -- a cerium -- 30at(s)% -- it considered as the mixed oxide of the cerium oxide and indium oxide which are included. a silver system thin film -- copper -- 0.8at(s)% -- it considered as the included silver copper alloy. All form membranes in sputtering and carry out pattern formation in wet etching. The insulator layer 15 which is cerium oxide formed membranes in sputtering similarly. The sheet resistivity values of the three-layer electrode of this example were 2.8ohm/**, and the permeability in a glass reference (a medium is Ayr) was about 97% in 550nm.

[0026] both the naked eye after keeping the electrode substrate of this example under 60 degrees C and the environment of 95% of humidity for 200 hours, and a microscope -- when the appearance was investigated by the method, change was not produced at all. Resistance and permeability were also changeless. Although the electrode substrate which has not carried out the laminating of the insulator layer 15 was put on the bottom of this environment as an example of a comparison for 200 hours, when the appearance was investigated, silverfish and the defect of several micrometers - 20 micrometer size appeared here and there near the edge of a stripe pattern.
 [0027] <Example 2> the electrode plate 2 concerning this example As shown in drawing 1 (b), as the glass substrate 21 with a thickness of 0.7mm and a stripe pattern-like reflector The transparence oxide thin film 22 with a thickness of 10nm, the silver system thin film 23 with a thickness of 150nm, the transparence oxide thin film 24 with a thickness of 10nm, and the insulator layer 25 that is cerium oxide with a thickness of 40nm as the pattern of this three-layer electrode is covered were formed, and it considered as the electrode substrate for reflective mold liquid crystal displays. the transparence oxide thin films 22 and 24 -- each -- metallic element conversion (an oxygen element is not counted) -- a cerium -- 30at(s)% -- it considered as the mixed oxide of the cerium oxide and indium oxide which are included. a silver system thin film -- copper -- 0.8at(s)% -- it considered as the included silver copper alloy. Each of others and membrane formation approaches and pattern formation approaches is the same as that of an example 1. The sheet resistivity values of the three-layer electrode of this example were about 0.2ohm/**, and the reflection factor in a barium-sulfate reference was about 93% in 550nm.

[0028] both the naked eye after keeping the electrode substrate of this example under 60 degrees C and the environment of 95% of humidity for 200 hours, and a microscope -- when the appearance was investigated by the method, change was not produced at all. Resistance and permeability were also changeless. Although the electrode substrate which has not carried out the laminating of the insulator layer 15 was put on the bottom of this environment as an example of a comparison for 200 hours, when the appearance was investigated, silverfish and the defect of several micrometers - 20 micrometer size appeared here and there near the edge of a stripe pattern.

[0029] In addition, in an example 2, although thickness of an insulator layer 25 was set to 40nm, in order to harness the reflected light from the tooth space 26 between the patterns of a three-layer electrode, you may form around 50nm - 60nm still more thickly. By forming the cerium oxide of a high refractive index thickly, the reflected light component from other than the pattern section can increase, and further improvement in brightness of a reflective mold liquid crystal display can be aimed at. The substrate in which the cerium oxide of

50nm thickness was formed on the glass side has about 30 – 40% of reflection factor. In the substrate which did not form cerium oxide but the glass substrate exposed in parts other than a pattern on the other hand, it is 5 – 6% of reflection factor. On the contrary, in the case of a transparency mold liquid crystal display, it is necessary to stop the reflective component from the tooth-space section but, and if thickness of cerium oxide is set to 5nm or less and made to form, a reflection factor almost comparable only as a glass substrate can be obtained.
[0030]
[Effect of the Invention] According to this invention, moisture resistance can be improved, maintaining high permeability in a transparent electrode, in order to arrange an insulator layer with a larger refractive index than 2.1 on a three-layer electrode. Moreover, moisture resistance can be improved in a reflector, with a high reflection factor maintained. Moreover, as an electrode substrate for reflective mold liquid crystal displays of the Nor Marie White display, since the reflection from for example, the tooth-space section of those other than an electrode pattern is also expectable, further improvement in brightness is achieved. Moreover, since a part of thickness of a transparence oxide thin film can be replaced with cerium oxide, the amount of the expensive indium oxide used can be reduced.
[0031]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the sectional view of the electrode substrate concerning [concerning an example 1 in (a)] an example 2 in (b), respectively.
[Drawing 2] It is the sectional view showing an example of the transparent electrode plate used for a liquid crystal display.
[Drawing 3] It is the graph which shows the spectral reflectance and spectral transmittance at the time of changing the refractive index of a transparence oxide thin film of the electrode substrate concerning this invention.
[Drawing 4] In the simulation of an electrode substrate, it is the graph which shows the difference of the spectral characteristic at the time of being a time of the refractive index of a medium being 1, and 1.5.
[Drawing 5] It is the graph which shows the spectral characteristic at the time of changing the thickness of a silver system thin film of the electrode substrate concerning this invention in a thin field.
[Drawing 6] It is the graph which shows the spectral characteristic at the time of changing the thickness of a silver system thin film of the electrode substrate concerning this invention in a thick field.
[Description of Notations]
11 21 : Substrate
12, 14, 22, 24 : Transparence oxide thin film
13 23 : Silver system thin film
15 25 : Insulator layer

[Translation done.]

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Ｇ０９Ｆ　9/30	３１５		Ｇ０９Ｆ　9/30	３１５	
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審査請求　有　請求項の数７　ＯＬ　（全７頁）

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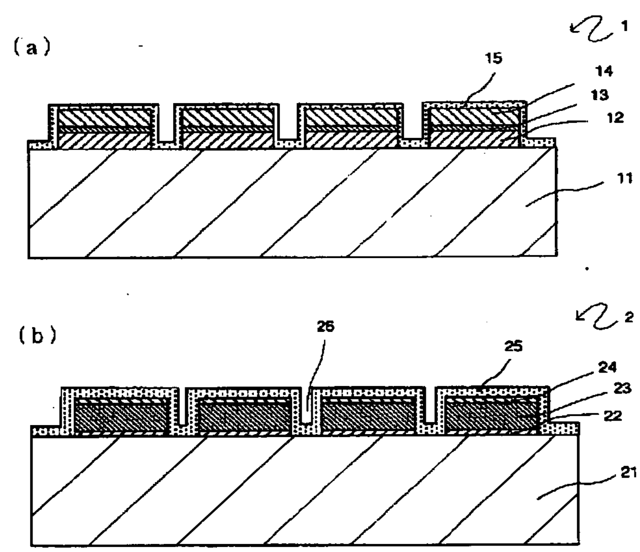
最終頁に続く

(54)【発明の名称】　電極基板

(57)【要約】
【課題】薄膜で導電性と可視光線透過率が高く、しかも経時劣化がなく保存安定性に優れた透明導電膜を提供する。
【解決手段】基板上に銀系薄膜を透明酸化物薄膜で挟持する構成の導電膜を備える電極基板において、上記導電膜上に屈折率が２．１より大きい絶縁膜を配設してなる。



【特許請求の範囲】

【請求項1】基板上に銀系薄膜を透明酸化物薄膜で挟持する構成の導電膜を備える電極基板において、上記導電膜上に屈折率が2．1より大きい絶縁膜を配設してなることを特徴とする電極基板。

【請求項2】上記絶縁膜の基材が酸化セリウムであることを特徴とする、請求項1記載の電極基板。

【請求項3】上記絶縁膜の膜厚が１ｎｍ～７０ｎｍの範囲にあることを特徴とする、請求項１または請求項２記載の電極基板。

【請求項4】上記銀系薄膜の膜厚が４ｎｍ～１７ｎｍの範囲にあることを特徴とする、請求項１、２または３記載の電極基板。

【請求項5】上記銀系薄膜の膜厚が５０ｎｍ～２００ｎｍの範囲にあることを特徴とする、請求項１、２または３記載の電極基板。

【請求項6】上記透明酸化物薄膜の基材が、酸化セリウムと酸化インジウムとの混合酸化物であることを特徴とする、請求項1、２、３、４または５記載の電極基板。

【請求項7】上記基板と導電膜との間にカラーフィルタが配設されていることを特徴とする、請求項1、２、３、４または6記載の電極基板。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、液晶ディスプレイ、入出力装置あるいはプラズマディスプレイ等の表示装置向け透明電極もしくは反射電極の電極基板、あるいは太陽電池用の透明電極もしくは反射電極に係わり、特に薄膜で導電性と可視光線透過率が高く、しかも保存安定性に優れた電極基板に関するものである。

【０００２】

【従来の技術】ガラス、プラスチックフィルム等の基板上に、可視光線を透過する電極形状の透明導電膜が設けられた電極板は、液晶ディスプレイ等の各種表示装置の表示用電極やこの表示装置の表示画面から直接入力する入出力電極などに広く使用されている。例えば、液晶が用いられたディスプレイ装置の透明電極板は、図２に示すように、ガラス基板３１と、このガラス基板３１上の画素部位に設けられ画素毎にその透過光を赤、緑、青にそれぞれ着色するカラーフィルタ層３７と、上記ガラス基板３１上の画素と画素との間の部位（画素間部位）に設けられこの部位からの光透過を防止する遮光膜３８と、上記カラーフィルタ層３７の全面に設けられた保護層３９と、この保護層３９上に成膜された透明電極４０と、この透明電極４０上に成膜された配向膜４１とでその主要部が構成されている。そして、上記透明電極４０はスパッタリングにより成膜され、所定のパターンにエッチングされた透明導電被膜により構成されている。

【０００３】この透明導電被膜としては、その高い導電性に着目して、酸化インジウム中に酸化錫を添加したＩ

ＴＯ薄膜が広く利用されており、その比抵抗はおよそ２．４×１０$^{-4}$Ω・cmで、透明電極として通常適用される２４０ｎｍの膜厚の場合、その面積抵抗率はおよそ１０Ω／□である。また、この他にも、酸化錫薄膜、この酸化錫に酸化アンチモンを添加して構成される薄膜（ネサ膜）、酸化亜鉛に酸化アルミニウムを添加して構成される薄膜などが知られているが、これらはいずれも上記ＩＴＯ薄膜よりその導電性が劣り、また、酸やアルカリに対する耐薬品性あるいは耐水性などが不十分なため一般には普及していない。

【０００４】一方、１９８２年日本で開催された第７回ＩＣＶＭにおいて、熱線反射膜として銀薄膜の表裏面にＩＴＯ薄膜または酸化インジウム薄膜（ＩＯ薄膜）を積層させて構成される３層構造の透明導電膜が提案されている。この３層構造の透明導電膜はおよそ５Ω／□程度の低い面積抵抗率を有しており、その高い導電性を生かして上記透明電極への応用が期待された。

【０００５】

【発明が解決しようとする課題】ところで、上記ディスプレイ装置や入出力装置においては、近年、画素密度を増大させて緻密な画面を表示することが求められ、これに伴って上記透明電極パターンの緻密化が要求されており、例えば１００μｍ程度のピッチで上記透明電極の端子部を構成することが要求されている。また、液晶ディスプレイ装置において基板に液晶駆動用ＩＣが直接接続される方式（ＣＯＧ）においては、配線の引き回しが幅２０～５０μｍという細線となる部分があり、従来にない高度のエッチング加工適性と高い導電性（低い抵抗率）が要求されている。

【０００６】また、その一方で表示画面の大型化も求められており、このような大画面化について上述したような緻密パターンの透明電極を形成し、しかも液晶に十分な駆動電圧を印加できるようにするためには、上記透明電極として５Ω／□以下という高い導電性を備えた透明導電膜を適用する必要があった。また、これに加えて、ＳＴＮ液晶等を利用した単純マトリクス駆動方式の液晶表示装置において１６階調以上の多階調表示を行う場合には３Ω／□以下というさらに低い面積抵抗率が要求されている。

【０００７】しかしながら、第７回ＩＣＶＭにおいて提案された上記３層構造の透明導電膜においても、高々５Ω／□程度の面積抵抗率が得られるに過ぎず、十分な導電性が確保できないという問題点があった。なお、銀薄膜の厚さを１６～１８ｎｍ程度に厚くすることによりその面積抵抗率を約３Ω／□に低下させることは可能であるが、可視光線透過率（特に波長６１０ｎｍ程度の長波長側の可視光線透過率）が７５％程度まで低下し、透明導電膜としての機能が損なわれてしまう。

【０００８】さらに、上記３層構造の透明導電膜においては、銀の薄膜が積層界面などから進入した空気中の水

分と化合しやすく、その表面に反応物を生成してシミ状の欠陥を生じ、例えば液晶表示装置の透明電極に適用した場合にはその表面に表示欠陥などを生じやすいという問題点があった。本発明はこのような問題点に着目してなされたものであって、その課題とするところは、薄膜で導電性と可視光線透過率が高く、しかも経時劣化がなく保存安定性に優れた透明導電膜を提供することにある。

【０００９】一方、太陽電池用透明電極においては、その製造プロセスの関係で水素プラズマ耐性を必要とする。このため、水素プラズマ耐性の高い酸化亜鉛を基材とする透明電極を用いることが一般的である。しかし、酸化亜鉛系の透明電極は、フッ素ドープしたものや、アルミナ添加したものでも抵抗値が高く、太陽電池用透明電極として４００ｎｍ～８００ｎｍとかなり厚い膜厚にて形成する必要があった。

【００１０】本発明者らは、これらの問題をほぼ解消しうる電極基板として、例えば、０．１～3at％銅を含有する銀系薄膜を透明酸化物薄膜で挟持する構成の導電膜を形成した電極基板を提案している。しかし、この構成は、ほぼ実用レベルにあるが耐湿性がやや不十分であった。銅を1at％含有する銀系薄膜を透明酸化物薄膜で挟持する構成の導電膜（以下、３層電極と略す）付き電極基板を、６０℃、９５％湿度の高温高湿環境下にて保管すると、およそ２００時間前後でパターンに微小のシミが発生してしまう問題があった。

【００１１】

【課題を解決するための手段】上述のような技術的課題に鑑みて本発明者らが鋭意検討を重ねたところ、高屈折率かつ耐薬品性に優れる絶縁膜を、保護膜として３層電極上に形成した構成が良い結果を得ることを発見した。屈折率については、保護膜に限らず、銀系薄膜を挟持する透明酸化物薄膜においても同様に高いことが好ましい。この傾向は、空気よりも屈折率の高い液晶材料（通常の液晶の屈折率は１．５～１．６程度）やカラーフィルタ（カラーフィルタの材料の屈折率は１．５を若干超える程度）と接する形態の３層電極の場合に顕著である。

【００１２】例えば、ガラス等の基板上に形成された３層電極の片側が空気である場合のシミュレーション結果を図４のＢ線で示すが、透過率Ｔはピークで９６％以上、反射率Ｒは１％に近いところまで下がる。ここでは基板側の透明酸化物薄膜の膜厚を４０ｎｍ、Ａｇ膜厚を１４ｎｍ、空気と接する側の透明酸化物薄膜の膜厚を４４ｎｍとした。透明酸化物薄膜の屈折率をＩＴＯとほぼ同じ２．０として計算した。しかし、３層電極上にポリイミドの配向膜を４０ｎｍ積層し、これに接する液晶の屈折率を１．５として計算し直すと、図４のＡに示すように透過率Ｔと反射率Ｒはかなり悪くなる。透過率のピークは９０％を下回り、反射率Ｒは、光の波長５５０ｎｍ付近でおよそ１０％まで上昇してしまう。

【００１３】本発明者らは、このことから、３層電極に液晶の配向膜としてのポリイミド膜と液晶が接する形での計算を、透明酸化物薄膜の屈折率を変えて（屈折率を変えると同時に銀系薄膜を挟持する透明酸化物薄膜の膜厚も調整し、ほぼ最適化した）行った。結果を図３に示す。透明酸化物薄膜の屈折率が高い方が、特に２．１を超えると透過率が向上し、また、反射率も低下することがわかる。

【００１４】このように、本発明者らは、３層電極において、銀系薄膜の膜厚に対応して透明酸化物薄膜の膜厚を調整することによって、その透過率の最適化が可能であることを見出している。本発明者らはさらに、この透明酸化物薄膜は、一部を高屈折率の絶縁膜によって置き換えることが可能であることを発見した。絶縁膜による置き換えで３層電極の信頼性が大きく向上することを併せて発見した。すなわち、請求項１に係わる発明は、基板上に銀系薄膜を透明酸化物薄膜で挟持する構成の導電膜を備える電極基板において、上記導電膜上に屈折率が２．１より大きい絶縁膜を配設してなることを特徴とする電極基板である。

【００１５】酸化セリウムは、強い耐アルカリ性をもつと同時に、約２．５の極めて高い屈折率をもつ。透明酸化物薄膜の膜厚の一部を代替する形で、酸化セリウムを基材とする絶縁膜を用いることができる。すなわち請求項２に係わる発明は、絶縁膜の基材が酸化セリウムであることを特徴とする、請求項１記載の電極基板である。酸化セリウムには、耐酸、耐アルカリ性に富む酸化タンタルや酸化ガリウム、酸化錫など他の金属（あるいは半金属）の酸化物を添加しても良い。

【００１６】絶縁膜の形成は、その膜厚を１ｎｍ～７０ｎｍの範囲に設定することが適切である。１ｎｍより薄くても良いが、成膜時の膜厚制御及び３層電極の欠陥部を埋める効果（３層電極は微小欠陥があると、これを起点として水分などによりその構成が破壊されやすい）をあわせ考慮すると、１ｎｍが少なくとも必要である。３層電極の透明酸化物薄膜の片側の膜厚は、透過率や反射率を考慮するとおおむね２０ｎｍ～７０ｎｍの範囲から選択される。絶縁膜での透明酸化物薄膜の代替を行うとして、絶縁膜の最大膜厚は７０ｎｍでよい。すなわち、請求項３に係わる発明は、絶縁膜の膜厚が１ｎｍ～７０ｎｍの範囲にあることを特徴とする請求項１または２記載の電極基板である。

【００１７】本発明者らは、さらに深く研究を重ねた結果、透明酸化物薄膜の屈折率を高くしていった場合において、銀系薄膜の膜厚に適切な範囲があることを見出した。透明酸化物薄膜の屈折率を２．３とし、ガラス基板（ｎ＝１．５）側の透明酸化物薄膜の膜厚を３５ｎｍ、銀系薄膜の膜厚を１２ｎｍ、上層の透明酸化物薄膜の膜厚を３７ｎｍ、ポリイミド膜の膜厚を４０ｎｍ、媒質

（液晶を想定）の屈折率を１．５とした場合のシミュレーション結果を図５に示した。銀系薄膜の膜厚の薄い方が透過率が高く、反射率は低くなり、良い傾向を示している。銀系薄膜の膜厚が１７ｎｍより厚くなると、光の波長５５０ｎｍでの透過率は９０％以上を維持することが難しくなり、１７ｎｍより薄く形成する必要のあることがわかる。また、銀系薄膜は４ｎｍより薄くすると、実際上、均質な膜が形成されにくく、島状の着膜となる。４ｎｍより薄いと、こうした理由で反射率が増加するため銀系薄膜の膜厚は４ｎｍより厚くすることが望ましい。なお、透過型ＬＣＤを前提として、高輝度の光源をバックライトとする構成では、むろん１７ｎｍより銀系薄膜を厚く形成しても良い。すなわち、請求項４に係わる発明は、銀系薄膜の膜厚が４ｎｍ〜１７ｎｍの範囲にあることを特徴とする、請求項１、２または３記載の電極基板である。

【００１８】また、３層電極において、銀系薄膜の膜厚を５０ｎｍより厚く形成すると、光の反射率の高い反射電極となる。反射電極は、反射型液晶表示装置で反射板と駆動電極を兼ねた反射電極として、あるいは太陽電池で、光電変換効率を高めるため半導体素子裏面に形成する光の反射膜として用いることができる。図６は、媒質の屈折率を１．５、透明酸化物薄膜の屈折率を２．３、膜厚を４０ｎｍにて、銀系薄膜の膜厚を５０ｎｍ、７５ｎｍ、１００ｎｍ、２００ｎｍとしてシミュレーションしたものである。銀系薄膜の膜厚が５０ｎｍを超えると８０％前後の反射性電極となり、２００ｎｍで反射率が飽和し、透過率もほぼ０％となることが示されている。すなわち、請求項５に係わる発明は、銀系薄膜の膜厚が５０ｎｍ〜２００ｎｍの範囲にあることを特徴とする、請求項１、２または３記載の電極基板である。

【００１９】なお、反射電極を形成する基板は、透明であっても良いが、白、黒その他の色に着色された基板であっても良い。材質も、ガラス、プラスチックフィルム、セラミック、金属あるいはアモルファスシリコンの半導体素子が形成された基板など、種々のものが使用できる。

【００２０】ところで、［ＩＴＯ／Ａｇ／ＩＴＯ］の構成に代表される従来の３層電極は、耐湿性に大きな問題がある。また、ＩＴＯは屈折率が１．８〜２．０程度であるため、高性能の３層電極を提供できるものではない。本発明者らは、種々の酸化物を検討した結果、酸化セリウムと酸化インジウムの混合酸化物を３層電極の透明酸化物薄膜として用いる構成が、耐湿性及び光学特性において極めて優れていることを見出した。すなわち、請求項６に係わる発明は、透明酸化物薄膜の基材が、酸化セリウムと酸化インジウムとの混合酸化物であることを特徴とする、請求項１、２、３、４または５記載の電極基板である。

【００２１】この混合酸化物による透明酸化物薄膜は、酸化物として含有する金属元素換算（酸素元素をカウントしない）で、セリウム元素を5at％以上、好ましくは２０at％以上、酸化インジウムに加えることにより、３層電極としてほぼ実用レベルの導電膜を備える電極基板を提供できる。３層電極としてパターン形成が必要な場合は、ウエットエッチングを前提とすると、セリウム元素の添加量は４０at％以下がよい。４０at％以上となると、ウエットエッチングでのパターン形成がやや難しくなる。４０at％以上の添加量でも、ドライエッチングの場合はこの問題はない。また、パターン形成が不必要な場合は、セリウム元素を４０at％を超えるレベルでの混合酸化物としても良い。透明酸化物薄膜の屈折率は、酸化セリウムの割合が高くなるにつれて高い屈折率となる。本発明者らのデータでは、セリウム２０at％でｎ＝２．１７、３０at％でｎ＝２．２４、４０at％でｎ＝２．３０、１００at％でｎ＝２．４９であった。なお、これら屈折率は成膜時の酸素ガスの分圧や成膜後のアニール温度条件などにより影響を受ける。

【００２２】本発明による電極基板は、表示装置用電極基板として用いる場合に、基板と透明電極である３層電極との間に、赤、緑、青などに着色されたカラーフィルタを配設することによりカラー表示を可能とする。すなわち、請求項７に係わる発明は、基板と導電膜との間にカラーフィルタが配設されていることを特徴とする、請求項１、２、３、４または６記載の電極基板である。

【００２３】

【発明の実施の形態】本発明の実施の形態を、以下の実施例に述べる。

【００２４】

【実施例】以下、本発明の実施例を図面を参照して詳細に説明する。

＜実施例１＞この実施例に係る電極基板１は、図１（ａ）に示すように、厚さ０．７mmのガラス基板１１と、ストライプパターン状の透明電極として厚さ４０ｎｍの透明酸化物薄膜１２と、厚さ１５ｎｍの銀系薄膜１３と、厚さ４０ｎｍの透明酸化物薄膜１４と、該３層電極のパターンを覆うように厚さ２ｎｍの酸化セリウムである絶縁膜１５を形成して、液晶表示装置向け電極基板とした。

【００２５】透明酸化物薄膜１２、１４はいずれも金属元素換算（酸素元素をカウントしない）でセリウムを３０at％含む、酸化セリウムと酸化インジウムの混合酸化物とした。銀系薄膜は銅を０．８at％含む銀銅合金とした。いずれもスパッタリングにて成膜し、ウエットエッチングにてパターン形成したものである。酸化セリウムである絶縁膜１５も同様にスパッタリングにて成膜した。当実施例の３層電極は、面積抵抗値が２．８Ω／□であり、また、ガラスレファレンス（媒質はエアー）での透過率は５５０ｎｍで約９７％であった。

【００２６】当実施例の電極基板を、６０℃、湿度９５

％の環境下に２００時間保管した後、肉眼、顕微鏡両方法にて外観を調べたところ、なんら変化は生じていなかった。抵抗値、透過率も変化がなかった。比較例として、絶縁膜１５を積層していない電極基板を同環境下に２００時間置いたものの外観を調べたところ、ストライプパターンのエッジ近傍に数μm～２０μmサイズのシミやディフェクトが散見された。

【００２７】<実施例２>この実施例にかかる電極板２は、図１（ｂ）に示すように、厚さ０．７mmのガラス基板２１と、ストライプパターン状の反射電極として、厚さ１０ｎｍの透明酸化物薄膜２２と、厚さ１５０ｎｍの銀系薄膜２３と、厚さ１０ｎｍの透明酸化物薄膜２４と、該３層電極のパターンを覆うように、厚さ４０ｎｍの酸化セリウムである絶縁膜２５とを形成して、反射型液晶表示装置向け電極基板とした。透明酸化物薄膜２２、２４は、いずれも金属元素換算（酸素元素をカウントしない）でセリウムを３０at％含む、酸化セリウムと酸化インジウムの混合酸化物とした。銀系薄膜は銅を０．８at％含む銀銅合金とした。他、成膜方法、パターン形成方法はいずれも実施例１と同様である。当実施例の３層電極は、面積抵抗値が約０．２Ω／□であり、また、硫酸バリウムレファレンスでの反射率は、５５０ｎｍで約９３％であった。

【００２８】当実施例の電極基板を、６０℃、湿度９５％の環境下に２００時間保管した後、肉眼、顕微鏡両方法にて外観を調べたところ、なんら変化は生じていなかった。抵抗値、透過率も変化がなかった。比較例として、絶縁膜１５を積層していない電極基板を同環境下に２００時間置いたものの外観を調べたところ、ストライプパターンのエッジ近傍に数μm～２０μmサイズのシミやディフェクトが散見された。

【００２９】なお、実施例２において、絶縁膜２５の膜厚を４０ｎｍとしたが、３層電極のパターン間のスペース２６からの反射光を活かすためには、さらに厚く５０ｎｍ～６０ｎｍ前後で形成しても良い。高屈折率の酸化セリウムを厚く形成することにより、パターン部以外からの反射光成分が増え、反射型液晶表示装置の更なる輝度向上を図ることができる。５０ｎｍ厚の酸化セリウムをガラス面上に形成した基板は、およそ３０～４０％の反射率を有する。一方、酸化セリウムを形成せず、パタ

ーン以外の部分でガラス基板が露出した基板では、５～６％の反射率である。逆に、透過型液晶表示装置の場合、スペース部からの反射成分を抑える必要があるが、酸化セリウムの膜厚を５ｎｍ以下にして形成せしめればガラス基板のみとほぼ同程度の反射率を得ることができる。

【００３０】

【発明の効果】本発明によれば、屈折率が２．１より大きい絶縁膜を３層電極上に配設するため、透明電極においては高透過率を維持したまま、耐湿性を向上することができる。また、反射電極においては、高反射率を維持したまま、耐湿性を向上することができる。また、ノーマリーホワイト表示の反射型液晶表示装置向け電極基板としては、電極パターン以外の、例えばスペース部からの反射も期待できるため、更なる輝度向上が図られる。また、透明酸化物薄膜の膜厚の一部を酸化セリウムで置き換えることができるため、高価な酸化インジウムの使用量を減らすことができる。

【００３１】

【図面の簡単な説明】

【図１】（ａ）は実施例１に、（ｂ）は実施例２に、それぞれ係わる電極基板の断面図である。

【図２】液晶表示装置に使用される透明電極板の一例を示す断面図である。

【図３】本発明に係わる電極基板の、透明酸化物薄膜の屈折率を変えた場合の分光反射率と分光透過率を示すグラフである。

【図４】電極基板のシミュレーションにおいて、媒質の屈折率が１であるときと１．５であるときの分光特性の差を示すグラフである。

【図５】本発明に係わる電極基板の、銀系薄膜の膜厚を薄い領域で変えた場合の分光特性を示すグラフである。

【図６】本発明に係わる電極基板の、銀系薄膜の膜厚を厚い領域で変えた場合の分光特性を示すグラフである。

【符号の説明】

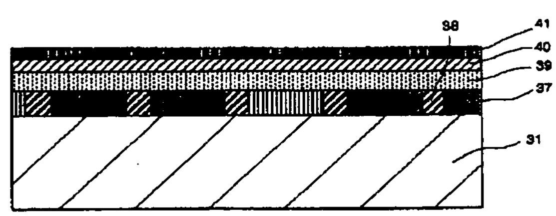
１１、２１：　基板

１２、１４、２２、２４：　透明酸化物薄膜

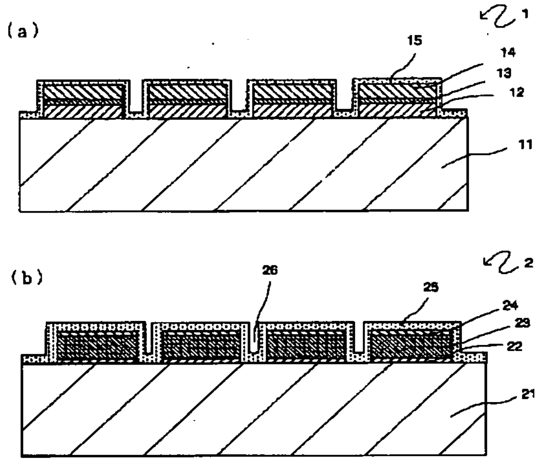
１３、２３：　銀系薄膜

１５、２５：　絶縁膜

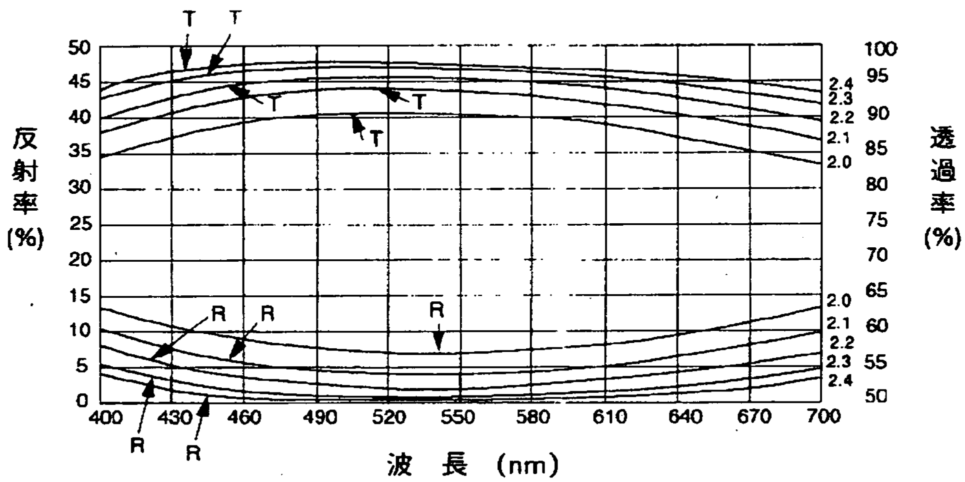
【図２】



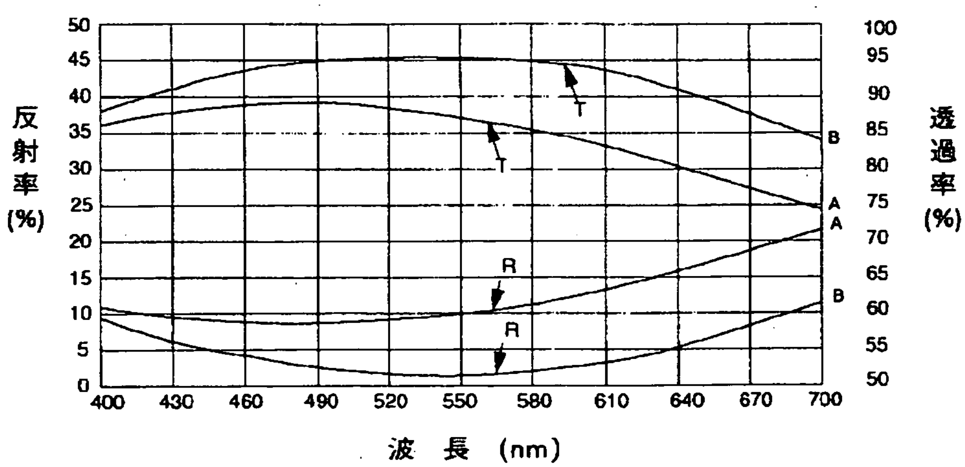
【図1】


(a)
1
15
14
13
12
11
(b)
2
26
25
24
23
22
21

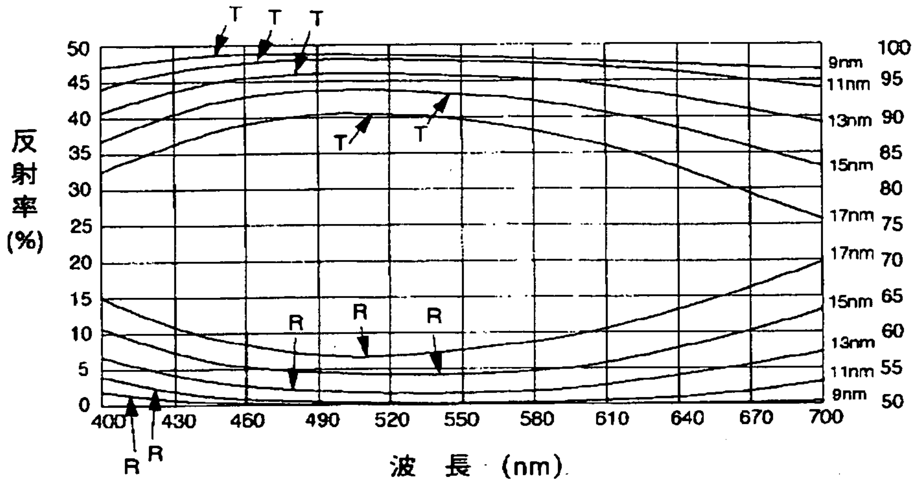
【図3】


反射率 (%)
透過率 (%)
波長 (nm)
T
R
2.4
2.3
2.2
2.1
2.0

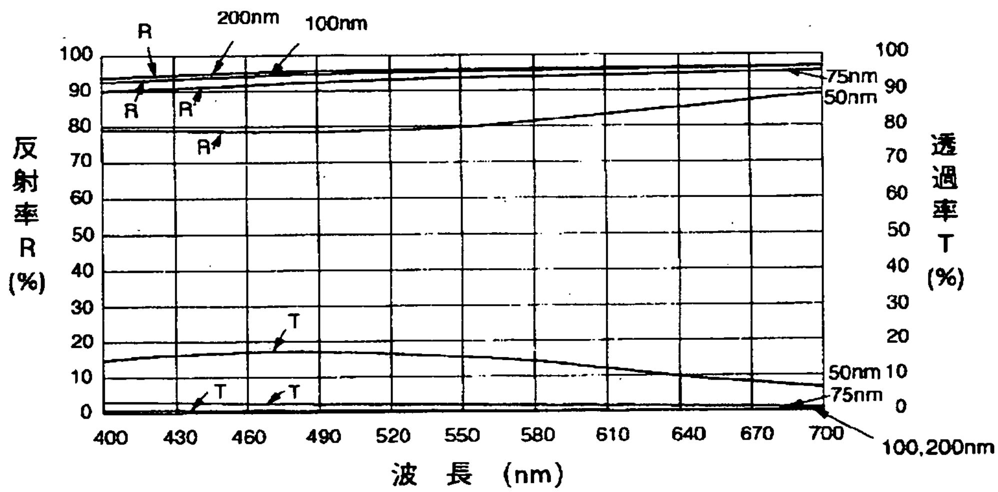
【図4】


反射率 (%)
透過率 (%)
波長 (nm)
T
R
A
B

【図5】



【図6】



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